

Poly[μ -chlorido-[μ_4 -5-(4-pyridyl)tetrazolato]dicopper(I)]

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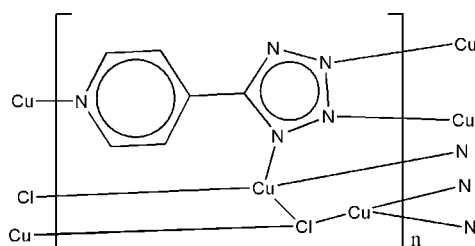
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.027; wR factor = 0.092; data-to-parameter ratio = 12.3.

The title three-dimensional coordination polymer, $[\text{Cu}_2\text{Cl}(\text{C}_6\text{H}_4\text{N}_5)]_n$, is the product of the hydrothermal reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and 5-(4-pyridyl)-1H-tetrazole (4-Hptz). The two independent Cu^{I} ions are coordinated in distorted tetrahedral and distorted trigonal coordination environments. In the unique 5-(4-pyridyl)-1H-tetrazolate ligand, the dihedral angle between the pyridine and tetrazole rings is 17.3 (2°).

Related literature

For related transition metals complexes of 5-(4-pyridyl)-1H-tetrazole, see: Xue *et al.* (2002); Jiang *et al.* (2004); Luo *et al.* (2005); Lin *et al.* (2005); Chen *et al.* (2008). For the applications of tetrazoles, see: Butler (1996).



Experimental

Crystal data

 $[\text{Cu}_2\text{Cl}(\text{C}_6\text{H}_4\text{N}_5)]$
 $M_r = 308.67$

 Monoclinic, Cc
 $a = 19.6899$ (7) Å

 $b = 3.64790$ (10) Å

 $c = 11.6337$ (3) Å

 $\beta = 102.923$ (2°)

 $V = 814.45$ (4) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 5.50$ mm⁻¹
 $T = 298$ K

 $0.30 \times 0.26 \times 0.24$ mm

Data collection

Bruker SMART APEXII

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\text{min}} = 0.230$, $T_{\text{max}} = 0.269$

3752 measured reflections

1572 independent reflections

 1415 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.092$
 $S = 1.11$

1572 reflections

128 parameters

2 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.71$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.71$ e Å⁻³

Absolute structure: Flack (1983),

621 Friedel pairs

Flack parameter: 0.19 (3)

Table 1

Selected geometric parameters (Å, °).

Cu1—N3 ⁱ	1.958 (5)	Cu2—N2 ⁱⁱⁱ	1.921 (5)
Cu1—N1	2.038 (5)	Cu2—N5 ^{iv}	1.931 (4)
Cu1—Cl1	2.4422 (15)	Cu2—Cl1	2.4923 (18)
Cu1—Cl1 ⁱⁱ	2.5090 (16)		
N3 ⁱ —Cu1—N1	133.4 (2)	N2 ⁱⁱⁱ —Cu2—N5 ^{iv}	152.3 (2)
N3 ⁱ —Cu1—Cl1	116.27 (15)	N2 ⁱⁱⁱ —Cu2—Cl1	101.13 (17)
N1—Cu1—Cl1	97.70 (14)	N5 ^{iv} —Cu2—Cl1	106.30 (16)
N3 ⁱ —Cu1—Cl1 ⁱⁱ	106.89 (15)	Cu1—Cl1—Cu2	123.48 (7)
N1—Cu1—Cl1 ⁱⁱ	100.51 (13)	Cu1—Cl1—Cu1 ⁱⁱⁱ	94.90 (6)
Cl1—Cu1—Cl1 ⁱⁱ	94.90 (6)	Cu2—Cl1—Cu1 ⁱⁱⁱ	78.17 (5)

 Symmetry codes: (i) $x, -y + 2, z - \frac{1}{2}$; (ii) $x, y + 1, z$; (iii) $x, y - 1, z$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Data collection: APEX2 (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXL97.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2752).

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supporting information

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Poly[μ -chlorido- $[\mu_4$ -5-(4-pyridyl)tetrazolato]dicopper(I)]**Cun-Kuan Wang and Xiao-Yan Li****S1. Comment**

Tetrazoles have found a wide range of applications in areas as diverse as coordination chemistry, medicinal chemistry and materials science (Butler, 1996). The study of complexes containing substituted tetrazole ligands is of interest to delineate the ways in which tetrazoles bind to metal centres. Recently, a series of 5-(4-pyridyl)-1*H*-tetrazole complexes of transition metals have been reported in which a range of coordination modes for the ligand were observed and extended two-dimensional and three-dimensional structures identified (Xue *et al.*, 2002; Jiang *et al.*, 2004; Luo *et al.*, 2005; Lin *et al.*, 2005; Chen *et al.*, 2008). Herein, we report the crystal structure of a three-dimensional coordination polymer, $[\text{Cu}^{\text{I}}_2\text{Cl}(4\text{-ptz})]_n$, derived from 5-(4-pyridyl)-1*H*-tetrazole and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ under hydrothermal reaction.

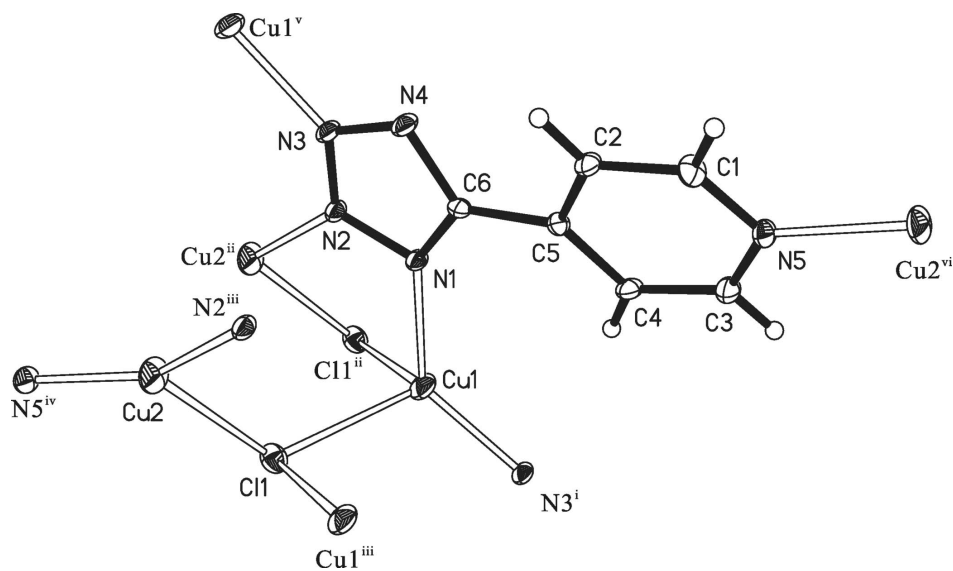
The asymmetric unit of the title complex contains of two independent Cu^{I} ions, one Cl^- , and one 4-ptz ligand. As shown in Fig. 1, atom Cu1 adopts distorted tetrahedral geometry with a Cl_2N_2 donor set and atom Cu2 is in a distorted trigonal coordination geometry with an N_2Cl donor set. Atom Cl1 is bonded to three Cu^{I} atoms, and the 4-ptz ligand coordinates to four Cu^{I} ions. It is noteworthy that atoms N1, N2, and N3 bond to three Cu^{I} atoms, respectively, forming a μ_3 -1,2,3-tetrazolyl coordination mode. The overall structure of title complex is a three-dimensional network (Fig. 2).

S2. Experimental

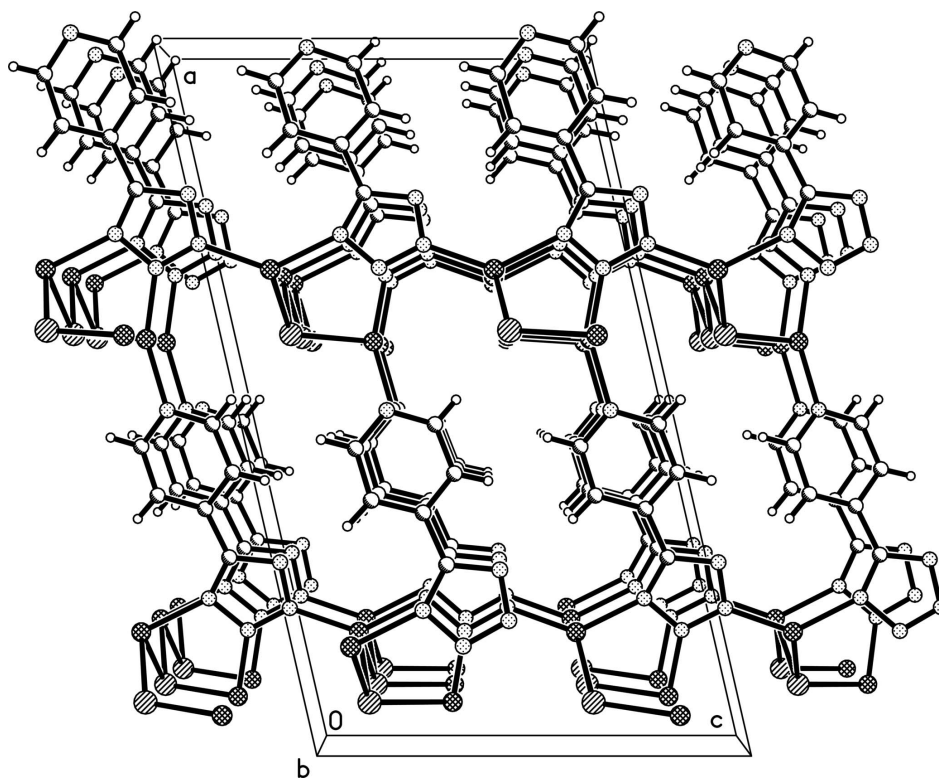
A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.172 g, 1 mmol), 5-(4-pyridyl)-1*H*-tetrazole (0.074 g, 0.5 mmol) in 8 ml deionized water was homogenized at room temperature for 30 minutes. Then the final solution was sealed in a 20 mL stainless-steel autoclave at 433 K for 72 h. A quantity of crystals was obtained after the solution was cooled to room temperature. The crystals were filtered, washed with deionized water and dried at room temperature. The yield is *ca* 64% based on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$.

S3. Refinement

All H atoms on C atoms were positioned geometrically and allowed to ride on their respective parent atoms, with $\text{C}-\text{H} = 0.93$ and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The crystal is an inversion twin with the ratio of twin components 0.81 (3):0.19 (3).

**Figure 1**

View of the coordination environment around the Cu^{I} ions and 4-ptz ligand of title complex with labeling scheme and 30% thermal ellipsoids. Symmetry codes: (i) $x, -y + 2, z - 1/2$; (ii) $x, y + 1, z$; (iii) $x, y - 1, z$; (iv) $x - 1/2, y - 1/2, z$; (v) $x, -y + 2, z + 1/2$; (vi) $x + 1/2, y + 1/2, z$.

**Figure 2**

Part of the crystal structure of the title complex.

Poly[μ -chlorido- $[\mu_4$ -5-(4-pyridyl)tetrazolato]dicopper(I)]

Crystal data

[Cu₂Cl(C₆H₄N₅)] $M_r = 308.67$ Monoclinic, *Cc*

Hall symbol: C -2yc

 $a = 19.6899$ (7) Å $b = 3.6479$ (1) Å $c = 11.6337$ (3) Å $\beta = 102.923$ (2)° $V = 814.45$ (4) Å³ $Z = 4$ $F(000) = 600$ $D_x = 2.517$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1367 reflections

 $\theta = 2.1$ – 27.8 ° $\mu = 5.50$ mm⁻¹ $T = 298$ K

Block, yellow

 $0.30 \times 0.26 \times 0.24$ mm

Data collection

Bruker SMART CCD APEXII

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.40 pixels mm⁻¹ ω scans

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\min} = 0.230$, $T_{\max} = 0.269$

3752 measured reflections

1572 independent reflections

1415 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.027$ $\theta_{\max} = 27.8$ °, $\theta_{\min} = 2.1$ ° $h = -21 \rightarrow 25$ $k = -4 \rightarrow 4$ $l = -15 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.027$ $wR(F^2) = 0.092$ $S = 1.11$

1572 reflections

128 parameters

2 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0547P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.71$ e Å⁻³ $\Delta\rho_{\min} = -0.71$ e Å⁻³

Absolute structure: Flack (1983), 621 Friedel

pairs

Absolute structure parameter: 0.19 (3)

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.17283 (4)	0.9867 (2)	0.16168 (5)	0.0302 (2)
Cu2	0.07924 (5)	0.1504 (3)	0.34304 (8)	0.0341 (2)

Cu1	0.08796 (8)	0.4991 (4)	0.16267 (13)	0.0264 (3)
N1	0.2207 (2)	0.9667 (13)	0.3361 (4)	0.0188 (9)
N2	0.1753 (3)	1.0294 (14)	0.4064 (5)	0.0209 (9)
N3	0.2072 (3)	0.9615 (14)	0.5171 (4)	0.0219 (10)
N4	0.2723 (3)	0.8552 (15)	0.5223 (4)	0.0232 (10)
N5	0.4827 (2)	0.6742 (14)	0.3528 (4)	0.0215 (10)
C1	0.4640 (3)	0.5674 (16)	0.4514 (6)	0.0234 (12)
H1A	0.4971	0.4535	0.5101	0.028*
C2	0.3980 (3)	0.6184 (16)	0.4700 (5)	0.0203 (11)
H2A	0.3876	0.5450	0.5407	0.024*
C3	0.4326 (3)	0.8253 (16)	0.2677 (5)	0.0230 (11)
H3A	0.4446	0.9003	0.1985	0.028*
C4	0.3644 (3)	0.8755 (16)	0.2771 (5)	0.0203 (11)
H4A	0.3312	0.9704	0.2145	0.024*
C5	0.3469 (3)	0.7798 (14)	0.3829 (5)	0.0176 (10)
C6	0.2791 (3)	0.8611 (16)	0.4091 (5)	0.0173 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0279 (4)	0.0496 (4)	0.0144 (3)	-0.0021 (4)	0.0076 (3)	0.0018 (3)
Cu2	0.0125 (3)	0.0561 (5)	0.0334 (4)	0.0066 (4)	0.0042 (3)	0.0033 (4)
Cu1	0.0223 (7)	0.0274 (6)	0.0276 (8)	-0.0018 (5)	0.0016 (6)	0.0035 (5)
N1	0.012 (2)	0.032 (2)	0.012 (2)	0.0020 (18)	0.0023 (17)	0.0003 (18)
N2	0.013 (2)	0.036 (2)	0.014 (2)	0.0013 (19)	0.0042 (16)	-0.001 (2)
N3	0.017 (2)	0.038 (3)	0.011 (2)	0.0014 (19)	0.0038 (18)	-0.0001 (18)
N4	0.018 (2)	0.040 (3)	0.011 (2)	0.004 (2)	0.0035 (18)	0.001 (2)
N5	0.014 (2)	0.028 (2)	0.022 (2)	0.0037 (19)	0.0043 (19)	-0.0005 (19)
C1	0.016 (3)	0.028 (3)	0.025 (3)	0.006 (2)	0.001 (2)	0.006 (2)
C2	0.019 (3)	0.030 (3)	0.012 (3)	0.002 (2)	0.003 (2)	0.002 (2)
C3	0.017 (3)	0.034 (3)	0.018 (3)	0.002 (2)	0.005 (2)	-0.001 (2)
C4	0.021 (3)	0.028 (3)	0.012 (3)	0.004 (2)	0.002 (2)	-0.002 (2)
C5	0.012 (2)	0.023 (2)	0.017 (3)	0.002 (2)	0.002 (2)	-0.0028 (19)
C6	0.014 (2)	0.024 (2)	0.012 (2)	0.000 (2)	0.0001 (19)	-0.002 (2)

Geometric parameters (Å, °)

Cu1—N3 ⁱ	1.958 (5)	N4—C6	1.354 (7)
Cu1—N1	2.038 (5)	N5—C1	1.339 (8)
Cu1—C11	2.4422 (15)	N5—C3	1.349 (7)
Cu1—C11 ⁱⁱ	2.5090 (16)	N5—Cu2 ^{vi}	1.931 (4)
Cu2—N2 ⁱⁱⁱ	1.921 (5)	C1—C2	1.377 (8)
Cu2—N5 ^{iv}	1.931 (4)	C1—H1A	0.9300
Cu2—C11	2.4923 (18)	C2—C5	1.389 (8)
C11—Cu1 ⁱⁱⁱ	2.5090 (16)	C2—H2A	0.9300
N1—C6	1.325 (7)	C3—C4	1.383 (8)
N1—N2	1.360 (7)	C3—H3A	0.9300
N2—N3	1.323 (7)	C4—C5	1.395 (8)

N2—Cu2 ⁱⁱ	1.921 (5)	C4—H4A	0.9300
N3—N4	1.327 (7)	C5—C6	1.464 (7)
N3—Cu1 ^v	1.958 (5)		
N3 ⁱ —Cu1—N1	133.4 (2)	C1—N5—C3	116.8 (5)
N3 ⁱ —Cu1—C11	116.27 (15)	C1—N5—Cu2 ^{vi}	120.1 (4)
N1—Cu1—C11	97.70 (14)	C3—N5—Cu2 ^{vi}	122.9 (4)
N3 ⁱ —Cu1—C11 ⁱⁱ	106.89 (15)	N5—C1—C2	123.1 (5)
N1—Cu1—C11 ⁱⁱ	100.51 (13)	N5—C1—H1A	118.5
C11—Cu1—C11 ⁱⁱ	94.90 (6)	C2—C1—H1A	118.5
N2 ⁱⁱⁱ —Cu2—N5 ^{iv}	152.3 (2)	C1—C2—C5	119.8 (5)
N2 ⁱⁱⁱ —Cu2—C11	101.13 (17)	C1—C2—H2A	120.1
N5 ^{iv} —Cu2—C11	106.30 (16)	C5—C2—H2A	120.1
Cu1—C11—Cu2	123.48 (7)	N5—C3—C4	124.0 (5)
Cu1—C11—Cu1 ⁱⁱⁱ	94.90 (6)	N5—C3—H3A	118.0
Cu2—C11—Cu1 ⁱⁱⁱ	78.17 (5)	C4—C3—H3A	118.0
C6—N1—N2	104.9 (5)	C3—C4—C5	118.2 (5)
C6—N1—Cu1	142.2 (4)	C3—C4—H4A	120.9
N2—N1—Cu1	111.9 (4)	C5—C4—H4A	120.9
N3—N2—N1	108.7 (5)	C2—C5—C4	117.9 (5)
N3—N2—Cu2 ⁱⁱ	128.9 (4)	C2—C5—C6	118.6 (5)
N1—N2—Cu2 ⁱⁱ	122.1 (4)	C4—C5—C6	123.4 (5)
N2—N3—N4	110.1 (4)	N1—C6—N4	111.5 (5)
N2—N3—Cu1 ^v	129.6 (4)	N1—C6—C5	128.8 (5)
N4—N3—Cu1 ^v	120.3 (4)	N4—C6—C5	119.6 (5)
N3—N4—C6	104.8 (4)		

Symmetry codes: (i) $x, -y+2, z-1/2$; (ii) $x, y+1, z$; (iii) $x, y-1, z$; (iv) $x-1/2, y-1/2, z$; (v) $x, -y+2, z+1/2$; (vi) $x+1/2, y+1/2, z$.